



## Short communication

Symmetric cell evaluation of the effects of electrolyte additives on  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  nanocomposite anodes

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## HIGHLIGHTS

- Symmetric cell testing is an effective tool for battery material optimization.
- The optimal electrolyte additive for  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  is 2% vinylene carbonate.
- As the amount of additive increases, the electrolyte reduction potential increases.

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## ABSTRACT

Coulombic efficiency and capacity retention are some of the main issues with alloy anodes in lithium-ion batteries, and the use of electrolyte additives is a viable approach to overcome these problems. Accordingly, the effects of three electrolyte additives, viz., vinylene carbonate (VC), fluoroethylene carbonate (FEC), and vinylene carbonate (VEC), on the performance of a promising alloy anode material  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  have been investigated. With an aim to rapidly assess the effects of the electrolyte additives, symmetric cells fabricated with  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  were used. Symmetric cell testing showed results similar to those of conventional half-cell testing in as little as one-fifth of the time, illustrating that symmetric cell testing is a valuable tool for optimization the performance of battery materials. Among the various additives and concentrations investigated, 2% VEC was found to offer the best cell performance with the  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  nanocomposite anode.

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## 1. Introduction

Lithium-ion batteries have become the power source of choice for portable devices due to their higher energy density compared to other rechargeable systems. They are now being intensively pursued for transportation and grid storage applications. With an aim to lower the cost, cycle life, and energy and power density, there is immense interest to develop new electrode materials. One of the critical factors in the success of a new battery material is the time to market. The process of optimization and scale-up can be lengthy for a novel material coming from a research laboratory. The more techniques that are available for rapid optimization and screening of battery materials, the shorter the time to market can be and hence, the better the chances for commercial success with a new material. Good performance in terms of cycle life and safety are important for all batteries, but because of the nature of the

application, these two metrics are of even higher priority for materials that will be used in electric vehicles or for stationary storage.

The introduction of additives into the battery electrolyte is one method that has been used to improve the performance and increase the safety of lithium-ion batteries.

Electrolyte additives can reduce the impact of parasitic side reactions, solvent and salt ion degradation, lithium dendrite formation, and solid-electrolyte interphase (SEI) layer formation, thus extending the cycle life of the batteries [1–5]. Flame retardants have also been introduced as electrolyte additives for their ability to improve the safety of a battery in the event of fire [6–9].

Electrolyte additives rely on different chemical strategies to improve battery performance, and often it is hard to determine which ones will be effective at improving the performance of a new material. Adding complication to the optimization process, when a material has already shown stable performance over hundreds of cycles, it is not always practical to wait the length of time that it takes to gather cycle data on the long-term performance of a battery before doing another round of optimization. It is also

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impractical to monopolize a large number of cycling channel resources for months by simply running cells with many different additives at different volume percentages and seeing which one is best. For materials to make the leap from hundreds to tens of thousands of stable cycles, it is critical to develop ways in which to reduce the amount of time needed to see which additives are the most effective at improving the performance.

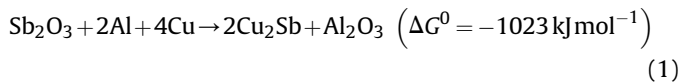
Symmetric cell testing is one method for making the battery optimization process more efficient. Symmetric cell testing has been used by several groups for fundamental lithium ion battery research and has been proposed as a tool for electrolyte optimization [10–15]. The symmetric cell technique eliminates variables from the battery system while magnifying the ability to observe losses from the electrode material that is being tested. In most symmetric cells, the electrodes are made of the same base material, but one of the electrodes has been pre-lithiated. Because the cell has electrodes made from the same material, any losses or improvements that are observed are only due to one electrode material. For symmetric cell testing with anode materials, the effects of the electrolyte additive on the counter electrode or the lithium metal electrode are eliminated. When lithium metal is used as the counter electrode, the losses due to the irreversible consumption of lithium may not be apparent for many cycles, whereas those losses are quickly observed in a symmetric cell arrangement because the amount of lithium in the system is fixed and much more limited than in a half cell.

The electrolyte additives chosen for this study were from the carbonate family. Vinylene carbonate (VC) has been used as an additive that increases the capacity retention of graphite anodes and is recommended for achieving the best battery performance with graphite. VC forms a surface polymer on the anode that has a higher conductivity than the normal SEI layer [16]. The surface polymer layer forms by reduction of VC before the ethylene carbonate (EC) in the electrolyte is reduced [5]. This polymerized VC-containing SEI layer suppresses further electrolyte and salt ion reduction [1]. Chen *et al.* [3] have reported that the SEI layer that contained VC was impermeable to the electrolyte. Fluoroethylene carbonate (FEC) and vinylene carbonate (VEC) have also been investigated as candidate additives because of their benefit to the performance of alloy anodes in the literature [17–27]. The mechanism for the beneficial effects of FEC on silicon anodes is still not well understood, but recent studies have suggested that FEC is transformed into VC, and then the VC subsequently polymerizes and provides a stable protective layer on the outside of the electrode, much like what is observed with the addition of VC to the electrolyte [18]. The influence of FEC in the electrolyte is to shift the reduction peak to a higher potential [22]. This shift to higher potential causes FEC to be reduced before the EC/DEC of the electrolyte. The reduction potential of VEC is even higher than that of FEC [22,25]. VEC has been examined as an electrolyte additive because it forms a passivating film on the electrode surface, but is more stable than VC [24,25]. Use of VEC electrolyte additives can also reduce the amount of gas evolved during cell operation [26]. Accordingly, we present here an investigation of the effects of the three electrolyte additives, viz., VC, VEC, and FEC, on the coulombic efficiency and voltage profile of the  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  nanocomposite alloy anodes in conventional half-cells and symmetric cells;  $\text{Cu}_2\text{Sb}$  has a theoretical capacity of  $323 \text{ mA h g}^{-1}$ , but the presence of  $\text{Al}_2\text{O}_3$  and C in the nanocomposite lowers the capacity of the overall anode.

## 2. Experimental

The  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  nanocomposite was synthesized by a reduction of  $\text{Sb}_2\text{O}_3$  (99.6%, Alfa) with aluminum (99.97%, 17  $\mu\text{m}$ ,

Alfa) and formation of  $\text{Cu}_2\text{Sb}$  with copper (99%, 45  $\mu\text{m}$  Acros Organics) metal powder in the presence of carbon (acetylene black) by a high-energy mechanical milling (HEMM) process, as illustrated below by reaction (1):



The overall negative free-energy change makes the reduction reaction (1) spontaneous. The required quantities of  $\text{Sb}_2\text{O}_3$ , Al, and Cu were mixed with acetylene black in an  $\text{Sb}_2\text{O}_3-\text{Al}-\text{Cu}:\text{C}$  weight ratio of 80:20. The HEMM was carried out in a planetary ball mill (Fritsch Pulverisette 6 planetary mill) for 12 h at a speed of 500 rpm at ambient temperature under argon atmosphere in a hardened steel vial having an 80  $\text{cm}^3$  capacity with steel balls (diameter: 1/2 and 1/4 in.) in a ball:powder weight ratio of 20 : 1. The vial was sealed inside an argon-filled glovebox prior to milling.

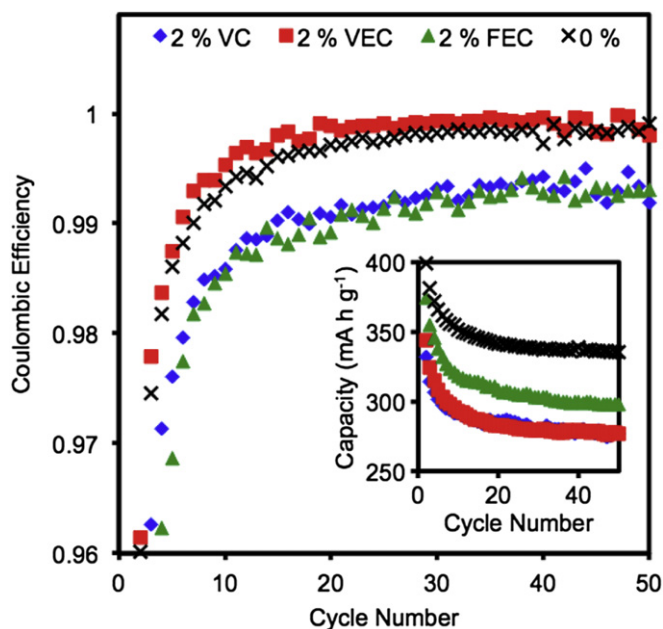
The electrodes for the electrochemical evaluation were prepared by mixing 70 wt.% material ( $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$ ) powder, 15 wt.% carbon black (Super P), and 15 wt.% polyvinylidene fluoride (PVDF) in *N*-methylpyrrolidone (NMP) to form a slurry. The slurry was spread onto a copper foil and dried at 120 °C for 2 h under vacuum. For the half cell preparation, the electrodes were then assembled into CR2032 coin cells in an Ar-filled glovebox using Celgard polypropylene separator, lithium foil as the counter electrode, and 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 v/v) electrolyte. For the symmetric cell preparation, a conventional half cell was assembled with a  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  electrode with approximately twice the area of a normal half cell. This  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  half cell with a larger electrode was then subjected to one conditioning cycle, followed by full lithiation. After full lithiation, the large  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  electrode was removed from its half cell and used as the counter electrode in a coin cell with a pristine  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  electrode and a layer of blown micro fiber polypropylene (BMF, 3 M) and Celgard separator material. The electrolytes with additives were prepared by adding the appropriate amount of VC (97% with <2% BHT, Aldrich), VEC (99%, Aldrich), and FEC (SynQuest Labs) by volume to 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 v/v). The discharge–charge experiments were performed galvanostatically at a constant current density of 100  $\text{mA g}^{-1}$  of active material within the voltage range of 0–2.0 V vs.  $\text{Li}/\text{Li}^+$  or 0.2 V–OCV vs.  $\text{Li}/\text{Li}^+$ . Cycle testing was performed at 25 °C.

## 3. Results and discussion

### 3.1. Half cell testing

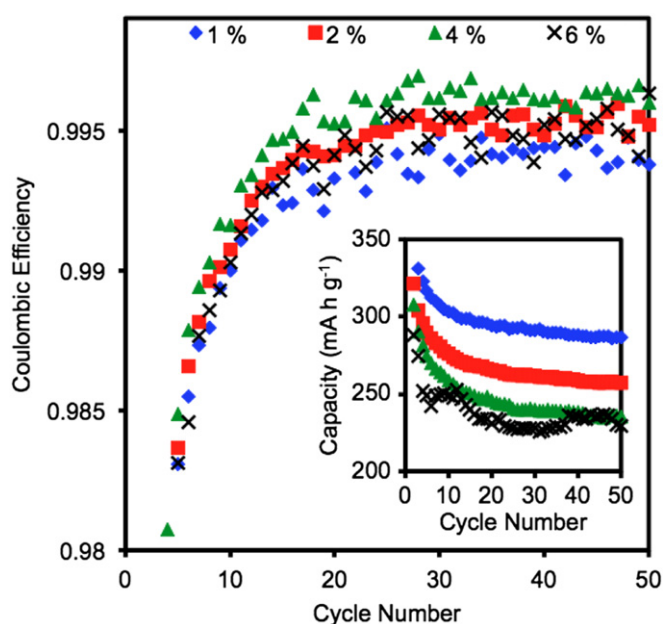
Initially, half cells were used to compare the effects 2% VC, 2% VEC, and 2% FEC electrolyte additives. Fig. 1 shows the coulombic efficiencies of half cells fabricated with and without 2% VC, VEC, and FEC additives. The 2% VEC cell shows the best coulombic efficiency of all of the cells tested. The discharge capacities of the cells with 2% electrolyte additives are shown in the inset in Fig. 1. The 2% FEC cell exhibits higher capacity than the other cells, but the capacity retention is poor as evidenced by the poor coulombic efficiency as well.

Because the half cells with 2% VEC showed the best coulombic efficiency out of the three additives, VEC was chosen for further optimization. Different amounts of VEC were introduced into the electrolyte and used to make a series of half cells with 1, 2, 4, 6, 8, and 10% VEC. Fig. 2 shows the coulombic efficiencies and discharge capacities (inset) of half cells fabricated with 1, 2, 4, and 6% VEC electrolyte additive. Above 6% VEC, the cycle performance was too poor to warrant any comparisons. In Fig. 2, the discharge capacity

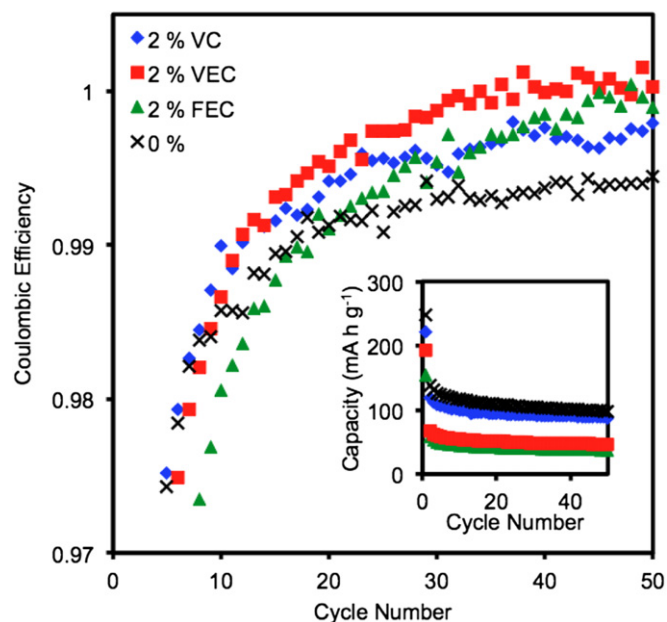


**Fig. 1.** Coulombic efficiency and cycle performance (inset) of  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  half-cells with 2% VC, 2% VEC, and 2% FEC at  $100 \text{ mA g}^{-1}$  and  $25^\circ\text{C}$  between 0 and 2 V vs.  $\text{Li/Li}^+$ .

of the half cell with 1% VEC is the highest among the four cells shown, but the coulombic efficiency of the cell with 1% VEC is the lowest of the four cells. The coulombic efficiencies of the cells with 2 and 4% VEC are virtually the same after 50 cycles. Because choosing the optimal amount of electrolyte additive is a balancing act between coulombic efficiency and discharge capacity, it was concluded that the half cells with 2% VEC exhibit the best overall performance. The half cells with 2% VEC have coulombic efficiencies similar to the half cells with 4% VEC, but the discharge capacity of the cells with 2% VEC are nearly  $25 \text{ mA h g}^{-1}$  higher than those with 4% VEC.



**Fig. 2.** Coulombic efficiency and cycle performance (inset) of  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  half-cells with 1, 2, 4, and 6% VEC at  $100 \text{ mA g}^{-1}$  and  $25^\circ\text{C}$  between 0 and 2 V vs.  $\text{Li/Li}^+$ .

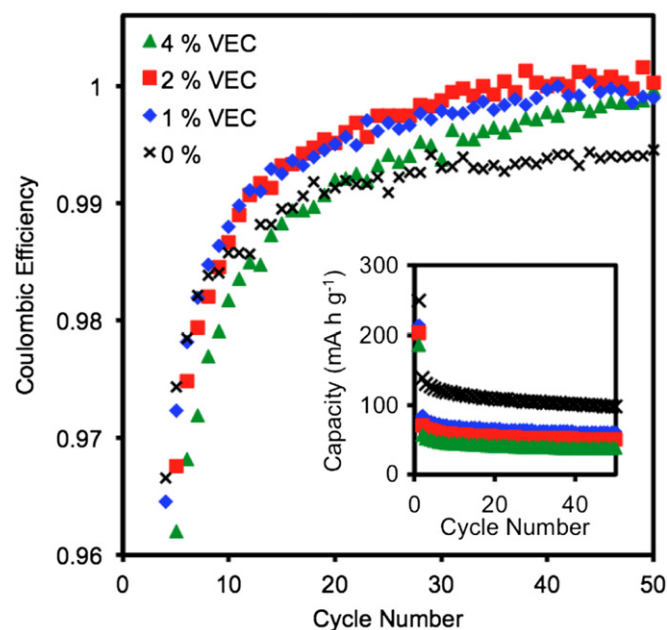


**Fig. 3.** Coulombic efficiency and cycle performance (inset) of  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  symmetric cells without and with 2% VC, 2% VEC, and 2% FEC at  $100 \text{ mA g}^{-1}$  and  $25^\circ\text{C}$  between 0 and 2 V vs.  $\text{Li/Li}^+$ .

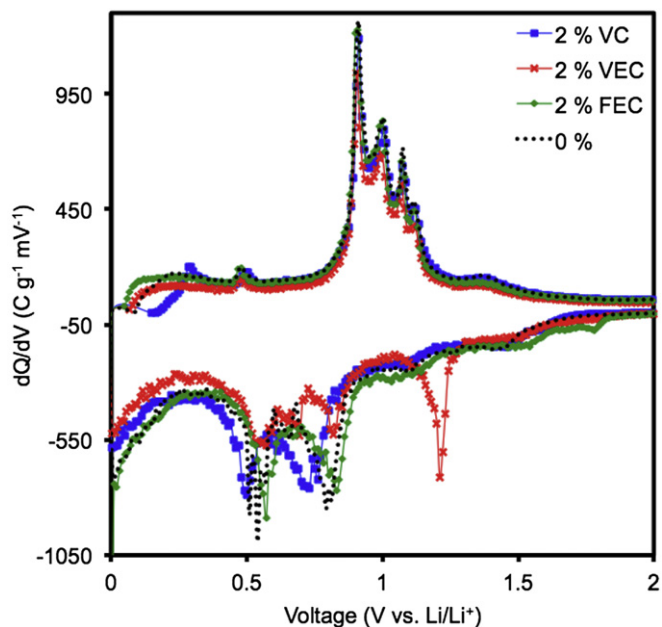
### 3.2. Symmetric cell testing

Because symmetric cell testing is viewed as a way to speed up the process of optimization, symmetric cells were made for experiments analogous to those performed with half cells. Fig. 3 shows the coulombic efficiencies of symmetric cells with and without 2% VC, 2% VEC, and 2% FEC additives. Of the three electrolyte additives, VEC shows the best performance in terms of coulombic efficiency.

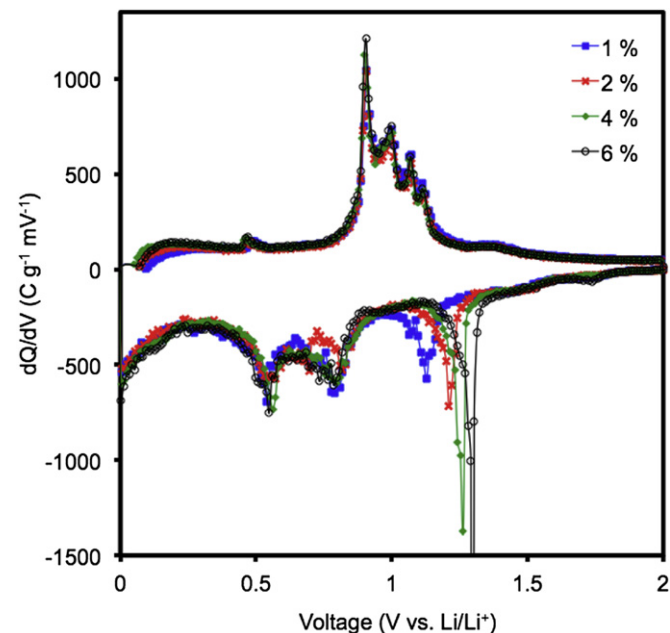
Fig. 4 shows the comparison between symmetric cells made with and without 1, 2, and 4% VEC. The symmetric cell with 2% VEC



**Fig. 4.** Coulombic efficiency and cycle performance (inset) of  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  symmetric cells without and with 1, 2, and 4% VEC at  $100 \text{ mA g}^{-1}$  and  $25^\circ\text{C}$  between 0 and 2 V vs.  $\text{Li/Li}^+$ .



**Fig. 5.** First cycle differential capacity plots (DCPs) of  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  half cells without and with 2% VC, 2% VEC, and 2% FEC at  $100 \text{ mA g}^{-1}$  and  $25^\circ\text{C}$  between 0 and 2 V vs.  $\text{Li/Li}^+$ .



**Fig. 7.** First cycle differential capacity plots (DCPs) of  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  half cells with 1, 2, 4, and 6% VEC at  $100 \text{ mA g}^{-1}$  and  $25^\circ\text{C}$  between 0 and 2 V vs.  $\text{Li/Li}^+$ .

shows the highest coulombic efficiency. In one fifth of the cycling time, symmetric cell testing confirmed the results that were obtained through half-cell testing with various electrolyte additives.

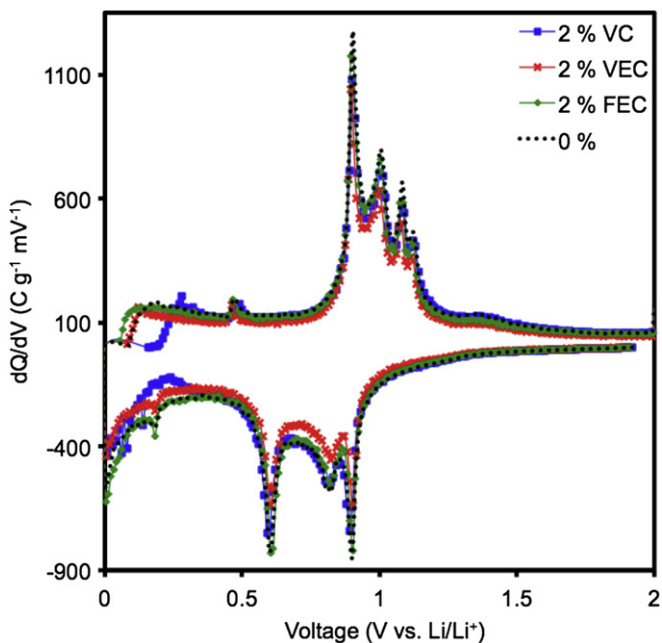
### 3.3. Comparison of reduction potentials

In order to better understand the effects of the electrolyte additives on the performance of the cells, differential capacity plots

(DCP) were made for each half cell. Fig. 5 compares the first cycle DCP of the cell without any electrolyte additive with those of cells with 2% VC, VEC, and FEC additives. The most striking feature of Fig. 5 is the peak that occurs for the cell with 2% VEC at  $\sim 1.2 \text{ V}$  vs.  $\text{Li/Li}^+$  in the lithiation (discharge) cycle. This peak corresponds to the reduction of VEC. The reduction reactions for VC and FEC appear in the DCP as a series of small peaks that occur at 1.5 and 1.1 V for VC and 1.8, 1.5, and 1.1 V for FEC. The reduction reactions for VC and FEC appear at potentials that are similar to the peaks for SEI formation from electrolyte decomposition in the cell with no additive present. The second cycle DCP for each of the three additives at 2% is shown in Fig. 6. All of the electrolyte reduction peaks do not appear in the second cycle. This indicates that the SEI layer has been formed during the first cycle and further electrolyte reduction is minimal. Furthermore, the amount of the electrolyte additive that is present in the cell can affect the potential at which the electrolyte is reduced [27]. Fig. 7 shows that as the amount of VEC increases, the reduction potential for the electrolyte also increases.

## 4. Conclusions

$\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  is known to show exceptional cycle life (500+ cycles) [28], and the incorporation of additives into the electrolytes is found in this study as a way to further optimize its electrochemical performance and minimize losses. Among the three additives (VC, VEC, and FEC) investigated with different concentrations, 2% VEC is found to offer the best cell performance with the  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  anode. Above 4% VEC, the cycle performance becomes less stable. Differential capacity plots reveal that as the amount of VEC additive is increased, the electrolyte reduction potential also increases, but too high a concentration of the additives sacrifices the discharge capacity. Furthermore, symmetric cell testing is found as an effective way for rapidly determining the effects of electrolyte additives on electrode materials for lithium-ion batteries; the symmetric cell testing can speed up the process of optimizing battery materials.



**Fig. 6.** Second cycle differential capacity plots (DCPs) of  $\text{Cu}_2\text{Sb}-\text{Al}_2\text{O}_3-\text{C}$  half cells without and with 2% VC, 2% VEC, and 2% FEC at  $100 \text{ mA g}^{-1}$  and  $25^\circ\text{C}$  between 0 and 2 V vs.  $\text{Li/Li}^+$ .

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